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LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA
DEPARTMENT OF PHYSICS
THE UNIVERSITY OF CHICAGO

TECHNICAL REPORT
for the period
1 April 1951 to 31 March 1952

PART ONE

Office of Naval Research
Contract N6ori-20, T.O. IX
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TABLE OF CONTENTS

(This Report is bound in two parts)

PART ONE

I. SUMMARY (included only in Part One)

1. Preface
2. Summary of Papers in Present Report
3. Shelter Island Conference on "Quantum-Mechanical Methods in Valence Theory"
4. Work in Progress
5. Associated Work

II. PAPERS ON MOLECULAR SPECTRA AND STRUCTURE

- Paper 1. Experimental Determination of Even-Odd Character of Excited Electronic States of Molecules with a Center of Symmetry. J. R. Platt
J. Chem. Phys., 19, 1418 (1951)
- Paper 2. Remarks on Spectra of Stilbene Derivatives. J. R. Platt
J. Am. Chem. Soc., 74, 2376 (1952)
- Paper 3. Prediction of Isomeric Differences in Paraffin Properties J. R. Platt
J. Phys. Chem., 56, 328 (1952)
- Paper A. Purification of Hydrocarbons for Use as Solvents in Far Ultraviolet Spectroscopy W. J. Potts, Jr.
J. Chem. Phys., 20, 809 (1952)
- Paper B. Catalysis of Cis-Trans Isomerization of Paramagnetic Substances H. McConnell
J. Chem. Phys., 20, 1043 (1952)
- Paper 4. Molecular Compounds and Their Spectra. III. The Interaction of Electron Donors and Acceptors. R. S. Mulliken
J. Phys. Chem., 56, 000 (1952)
- Paper 5. Overlap Integrals and Molecular Energies R. S. Mulliken
Record of Chemical Progress, 13, 000 (1952)
- Paper 6. Magic Formula, Structure of Bond Energies, and Isovalent Hybridization R. S. Mulliken
J. Phys. Chem., 56, 295 (1952)

- Item 7. ONR Report on Shelter Island Conference on "Quantum-Mechanical Methods in Valence Theory" (by title only; see Section 3 of Summary)
- Paper 8. On the Two-Center Exchange Integrals. . . . K. Rüdénberg
- Paper 9. On the Three- and Four-Center Integrals in Molecular Quantum Mechanics. . . . K. Rüdénberg
J. Chem. Phys., 19, 1433 (1951)
- Item 10. Corrigenda: A Study of Two-Center Integrals Useful in Calculations on Molecular Structure. I.C. C. J. Roothaan
- Item 11. Corrigenda: A Study of Two-Center Integrals Useful in Calculations on Molecular Structure. II. The Two-Center Exchange Integrals K. Rüdénberg

PART TWO

- Paper 12. On the Emission Bands of the NO Molecule in the Vacuum Ultraviolet RegionY. Tanaka
J. Chem. Phys., in press
- Paper 13. Spectra and Directing Forces in Substituted Aromatics. I. Fluorinated Benzenes.H. B. Klevens
and
L. J. Zimring
- Paper 14. Effect of Polar Solvents on the Absorption Frequency of $n-\pi$ Electronic Transitions H. McConnell
J. Chem. Phys., 20, 700 (1952)
- Paper 15. A Spectroscopic Study of the Benzene-s-Trinitrobenzene Molecular Complex . . .H. McConnell
J. Am. Chem. Soc., in press
and
D. M. G. Lawrey
- Paper 16. Complexes of Iodine with an Ether and an Alcohol.J. S. Ham, Jr.
J. Chem. Phys., 20, 000 (1952)
- Paper 17. Regularities in the Spectra of Molecular ComplexesJ. S. Ham, Jr.,
J. Chem. Phys., in press
J. R. Platt,
and
H. McConnell

Paper 18. Continuous Groups: Compact Groups. . .C. C. J. Roothaan

Paper 19. The Orthogonal Groups of Dimensions 2 and 3C. C. J. Roothaan

III. DISTRIBUTION LIST (included in both Part One and Two)

I. SUMMARY

1. Preface

Five previous comprehensive Technical Reports have been issued: a Quarterly Report for the period 1 June 1947 to 31 August 1947; an Annual Report (in two parts) for the period from 1 September 1947 to 31 August 1948; a Report (in two parts) for the period 1 September 1948 to 31 May 1949; a Report (in two parts) for the period 1 June 1949 to 31 March 1950; and a Report (in two parts) for the period 1 April 1950 to 31 March 1951. The present Report (also in two parts) brings the record up to date as of 31 March 1952. It includes: (a) complete texts of finished manuscripts and articles now in press or recently published, covering work partly or wholly supported by the contract and not included in previous Reports; (b) summaries of additional work in progress.

For an account of the general program and of available equipment, reference may be made to the Report for the period 1 September 1948 to 31 May 1949, Part I. In addition, the 21-foot vacuum spectrograph kindly given to us by Professor G. R. Harrison of the Massachusetts Institute of Technology has been in successful operation for nearly a year using an ordinary 15,000-line/inch speculum grating; a 30,000-line/inch grating ruled on an aluminum surface with the blaze at suitable angle has just been obtained from Bausch and Lomb, and we are looking forward to improved intensities with its use. Further, the Division of Physical Sciences has also recently purchased a Perkin-Elmer Model 120 Infrared Spectrophotometer to which we have access. A new Beckman IR3 Infrared Spectrophotometer is also available on campus for our use when needed.

2. Summary of Papers in Present Report

Paper 1 shows how one can determine whether the excited state of a symmetric aromatic molecule is even or odd by examination of the change of absorption intensity resulting from substitution in a substituted molecule. Paper 2 is an application of this theory to the spectra of stilbene derivatives recently studied by Beale and Roe, which permits one to establish unequivocally that the first excited state of stilbene is odd and that the intensity contributions for substitution at different positions are additive.

Paper 3 is a general examination of the problem of finding the best empirical formulas for the heats of formation, the molar volumes, boiling points, molar refractivities, and heats of vaporization of the isomeric paraffins through the octanes. Some "best" formulas are adopted which appear to predict all of these properties except the boiling points within experimental error.

Paper A describes a successful attempt to purify hydrocarbon solvents for the vacuum ultraviolet so that they transmit to $1,750\text{\AA}$ in $\frac{1}{8}$ -inch cells. They also form transparent glasses at liquid-nitrogen temperatures with a slight improvement in transmission. This work represents an extension of about 500\AA in the transmission limit of solvents for cells of this thickness.

In Paper B, McConnell proposes a new explanation of the catalysis of cis-trans isomerization by paramagnetic substances. He points out that the cause of the catalysis may be the fact that the spin ($\frac{1}{2}$) of the paramagnetic substance must cause mixing of the singlet ground state and excited triplet state wavefunctions during twisting of the molecule about a double bond. This mixing should permit cis-trans isomerization via the triplet state, which is believed to have a lower

energy at 90° twist than the singlet state.

Paper 4 by Mulliken contains a further development of ideas presented in earlier papers on molecular compounds and their spectra. An enlarged and refined classification of electron donors and acceptors into types is given. Examples of these and of their modes of interaction are tabulated. The interactions are in some cases dissociative (that is, a chemical displacement reaction occurs) and in others associative (a molecular complex or compound is formed). A listing of probable known charge-transfer spectra of molecular complexes is given. Finally, the formation by a donor-acceptor pair alternatively of an "outer complex" (a loose associative complex) or of an "inner complex" (usually an ion-pair structure), or sometimes of a "middle complex", is discussed.

Paper 5 is a review in simple style covering some of the earlier work by Mulliken on overlap integrals and chemical binding (see 1949-50 and 1950-51 Reports) and also some of the "magic formula" work (see Paper 6 of ~~this~~ Report), to which it forms a convenient introduction.

Paper 6 deals with a semi-empirical "magic formula" for bond energies, based on rough theoretical considerations derived from LCAO molecular orbital theory but transferred into the framework of valence-bond theory. This fits observed bond energies for a number of simple molecules within about $\pm 10\%$. Perhaps its chief interest, however, is the insight it gives into the various positive and negative terms which go to make up the total bond energy of any molecule. In particular, it indicates that (a) nonbonded repulsions, including those involving inner-shell electrons, are very important; (b) hybridization, often even in relatively small amounts, is very important in increasing bond strengths and in decreasing nonbonded repulsions; (c) π bonds are

exceedingly strong at short interatomic distances, as in N_2 or C_2H_2 where they are the essential bonding terms.

Concerning Item 7, see Section 3 of this Summary.

Paper 8 by Rudenberg on the two-center exchange integrals is based on the theory developed by the same author in a previous paper. The method of evaluation is elaborated for the essential, but very complicated, auxiliary functions, with the aim of standardizing the numerical work and facilitating it by a systematic arrangement. The proposed procedure has been successfully used by several coworkers. Paper 9 by the same author deals with the three- and four-center integrals, whose evaluation constitutes the last but also the most difficult integral problem to be solved. A new procedure is proposed in this first note. The method is being further elaborated and tested in cooperation with Professor Harrison Shull at Iowa State College, and it is hoped to give a more substantial account in the near future.

Items 10 and 11 are corrigenda for the articles published by Roothaan and Rudenberg in the December, 1951, JOURNAL OF CHEMICAL PHYSICS, which appeared under the title, "A Study of Two-Center Integrals Useful in Calculations on Molecular Structure." The corrigenda here presented pertain to the printed versions of these articles, and not to versions of the same articles which appeared in last year's Technical Report.

In Paper 12 by Tanaka, a report is made of his investigation of the NO emission spectrum in the far-ultraviolet region, using 35cm and 21-foot normal-incidence vacuum spectrographs. The existence of the ϵ -system is confirmed. The β' -bands are reinvestigated, and a curious appearance was observed in the (4,0) band. New bands which have an appearance similar to the β' -bands are observed in the region of $1,500\text{\AA}$, and tentative analysis is made.

Paper 13 reports the absorption spectra of a series of fluorinated benzenes to $1,700\text{\AA}$ with discussion of the theoretical implications of their wavelength shifts and intensity changes as different positions are substituted.

Paper 14 shows that the red shift or blue shift of absorption spectra in going from a nonpolar to a polar solvent is a reliable index of the transition type and is a qualitative measure of the change of dipole moment of the molecule in the excited state compared to the ground state.

In Paper 15 by Lawrey and McConnell, the establishment of a 1:1 molecular complex between benzene and *p*-trinitrobenzene is reported with an equilibrium constant of 4.1 in *n*-heptane solution. The spectrum of the complex is established down to $\lambda 2,100$.

Paper 16 records a study by J. S. Ham in which equilibrium constants are determined for molecular complexes of iodine with ethyl ether and with *t*-butyl alcohol, and identifications of ultraviolet peaks as charge-transfer spectra of the respective complexes are made.

Paper 17 presents two new empirical relations connecting wavelengths of the so-called charge-transfer spectra of molecular complexes with the ionization potentials of the donor molecule and showing its relative independence of the acceptor molecule. These data make untenable several theories of these spectra, and leave only two competing theories in the field of which the recent theory of Mulliken is more strongly favored.

Paper 18 gives a general--although not rigorous--analysis of the internal structure of *n*-parameter continuous groups, deriving in particular for compact groups the procedure of invariant integration, and establishing the orthogonality relations analogous to those for finite groups. In Paper 19, these matters are discussed extensively

for the special case of the orthogonal groups of dimensions 2 and 3. These two papers constitute the preliminary form of two chapters in a proposed textbook on group theory and its physical applications.

3. Shelter Island Conference

A conference on "Quantum-Mechanical Methods in Valence Theory", supported by the ONR through our project, was organized by Mr. Mulliken and held 7-10 September 1951 under the sponsorship of the National Academy of Sciences at Shelter Island, Long Island, New York. Messrs. Mulliken, Roothaan, and Rudenberg of our group took part in the conference, as did also Professors J. E. Mayer and G. W. Wheland of the Chemistry Department of the University of Chicago. Professors J. E. Lennard-Jones and C. A. Coulson, Dr. W. Hoffitt, and Mr. M. P. Barnett came from England, and Professor H. Kotani from Japan. Dr. L. E. Sutton of Oxford, England, and Dr. P.-O. Löwdin of Uppsala, Sweden, who were already in this country, also took part. Professor D. R. Hartree and Dr. H. C. Longuet-Higgins from England and Dr. R. Daudel from Paris were unable to attend. The remaining conference members came from this country.

Professor R. G. Parr of the Chemistry Department, Carnegie Institute of Technology, and Professor B. L. Crawford, Jr., of the Chemistry Department, University of Minnesota, who were among those present, acted as conference secretaries and have prepared a Summary of the conference for publication in the June, 1952, Proceedings of the National Academy of Sciences. Several other conference papers are being published in the March, April, May, and June, 1952, issues of the Proceedings. All the conference papers, formal and informal, together with discussion comments, Summary, and some additional previously published papers and numerical tables, so as to make up a unified whole, are being

issued soon as an ONR Report, of which copies may be obtained, while the supply lasts, from Mr. L. H. McKenzie, Head, Physics Branch, Office of Naval Research, Washington, D. C.

The ONR Report on the Shelter Island conference includes 54 separate papers and notes, plus some discussion comments. Reference should be made to that Report for several papers and notes which, because of their inclusion there, are omitted here. The following may be particularly noted; the numbers are those given to the papers in the ONR Shelter Island Report:

15. "Comments on the Meaning of Bond Orders", R. S. Mulliken.
25. "The Interaction of Electron Donors and Acceptors" (containing material largely but not entirely included in Paper 8 of 1950-1 Technical Report of this Laboratory and Paper 4 of present Report), R. S. Mulliken.
32. "A Comparative Summary of Approximate Ground State Wave Functions of Helium Atom and Hydrogen Molecule" (also in Proc. Nat. Acad. Sci., 38, 160 (1952)), R. S. Mulliken.
38. "On the Methods of Numerical Integration Used in Determining Self-Consistent Fields", P.-O. Löwdin.

4. Work in Progress

Work with the 21-foot vacuum grating spectrograph, supplemented by the 84-cm vacuum grating spectrograph, mainly on diatomic spectra (NO, NS, N_2^+ , etc.) is continuing actively (Tanaka, assisted by Schugrin). Experimental and theoretical work on molecular complexes and their spectra, and on other aspects of solution spectra is continuing.

Theoretical work on the evaluation of the two-center hybrid integrals is approaching completion (Rudenberg, Jaunzemis); pilot-plant calculations directed toward setting up the auxiliary functions of the

two-center exchange integrals for IBM computations are actively in progress (Rüdenberg, Kinyon). Arrangements for IBM computations on the two-center Coulomb integrals, to be carried out at the IBM center at Iowa State College, are being concluded (Roothaan). Other work on problems of molecular electronic structure, and on the interpretation of molecular electronic spectra, is continuing (Mulliken, Platt, Roothaan, Rüdenberg).

5. Associated Work

Dr. Harden McConnell, National Research Council Fellow, has been cooperating actively, especially in the work on spectra and structure of molecular complexes and on numerous aspects of solution spectra. His work has been in part jointly with ONR personnel or support, in part independent of ONR. (See Papers B, 14, 15, and 17).

Ph.D. students and AEC Predoctoral Fellows W. J. Potts, Jr., (Chemistry) and J. S. Ham (Physics) have been working respectively on low-temperature phosphorescence, fluorescence, and absorption spectra (see Paper A; further papers are in course of preparation), and on molecular complexes and their spectra in experiment and theory (see Papers 16, 17; Mr. Ham is continuing further work including low-temperature and infra-red spectra of molecular complexes).

Ph.D. students C. W. Scherr (Chemistry) and J. E. Faulkner (Physics) are carrying on quantum-mechanical studies on simple molecules (H_2 , Li_2). Mr. Scherr, making use of computational results obtained last fall by Dr. P.-O. Löwdin during his tenure as an ONR Research Associate, is also preparing a paper on a simplified approximate method of using self-consistent-field data which will appear in a later Technical Report of this Laboratory.